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A Detailed Voc Emission Inventory For The Assessment Of Their Contribution To Areosol Pollution

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1. Introduction

The PRAA (Environmental Action Plan 2004-2006 of the Tuscany Region, by ARPAT) emphasized the critical situation of the VOC pollution in the Leather District of Santa Croce (PISA, Italy) and underlined how this matter is caused by the use of solvent in the Tanning Industry. The VOC pollution is critical both for air quality by itself and because they are involved in photochemical pollution concerning ozone and particulate matter pollution.
This paper present the results of the study of the VOC pollution in the Leather District of Santa Croce (PISA, Italy) and is focused on the reconstruction of a detailed local emission inventory useful for air quality management representative of the local industrial background. This study was carried out in cooperation with Arpat of S.Romano , so that we are able to collect all the VOC related information about the types of products containing solvents, their quantities and related emissions by the Leather Company who had submitted the "Using Solvent Plan" according to the Directive 1999/13/CE (about the containment of industrial Organic Compound emission). All the collected and elaborated data were used to realized a geo-database that comprises detailed information about, emissions and chemical speciation of VOC from industrial sources.

1.1 Background

The Santa Croce sull'Arno district provides employment for over 80% of the total workforce in the manufacturing industry. The district is installed in the municipalities of Castelfranco di Sotto, Fucecchio, Montopoli in Val d'Arno, San Miniato, Santa Croce sull'Arno, Santa Maria a Monte (Fig.1) and alone accounts for 90% of Italy's production of real leather for footwear soles. The district has about 8.000 enterprises, of which 1.750 work in the tanning, footwear and leather sector.
Leather tanning is the process of converting raw hides or skins into leather. Tanning is essentially the reaction of collagen fibres in the hide with tannins, chromium, alum, or other chemical agents. The most common tanning agents used in the Santa Croce District are trivalent chromium and vegetable tannins extracted from specific tree barks.

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Emissions of VOC may occur during finishing processes, when organic solvents are used. Leathers may be finished in a variety of ways: buffed with fine abrasives to produce a suede finish; waxed, shellacked, or treated with pigments, dyes, and resins to

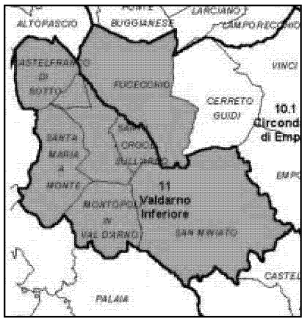

Figure 1 Leather District of Santa Croce sull'Arno

achieve a smooth, polished surface and the desired colour; or lacquered with urethane for a glossy patent leather. Water-based or solvent-based finishes may also be applied to the leather. Plating is then used to smooth the surface of the coating materials and bond them to the grain. Hides may also be embossed. Usually Voc emission are convoyed to chimney after drying in a abatement system with water with low reduction of organic compound which evaporate to the atmosphere; other control device, such as thermal oxidizers, aren't used again despite some tanneries use a quantity of organic compound which could allow to adopt it.

2. Methodology and Data Collection

As previously cited we developed a specific methodological approach for the Santa Croce District VOC's emissions study that is summarised in the following scheme, figure 2.

In our research we drew up a list including all Santa Croce Industrial Company who are submitted to European Directive 1999/13/CE, we localized and mapped them using Gis, to identify the single VOC source in the District Leather. The data collection is advanced according successively step:

- to archive all information collected from the Emission VOC Authorization (1999/13/CE) in a database. This database contained, for every tanneries: total VOC quantity introduced in the industrial process, type and annual quantity of every products purchased, number and description of chimney (geometrical data and mass flow of VOC's);
- to collect the safety data sheets and to identify the correct composition of every solvent;
- to transcript, on the database, the quantity of organic compound examined in the SAROAD 97 classification;

- to convert the VOC speciation for the CBIV Lumped Chemical Mechanism [1] so that the database can be used to apply chemical transport model.

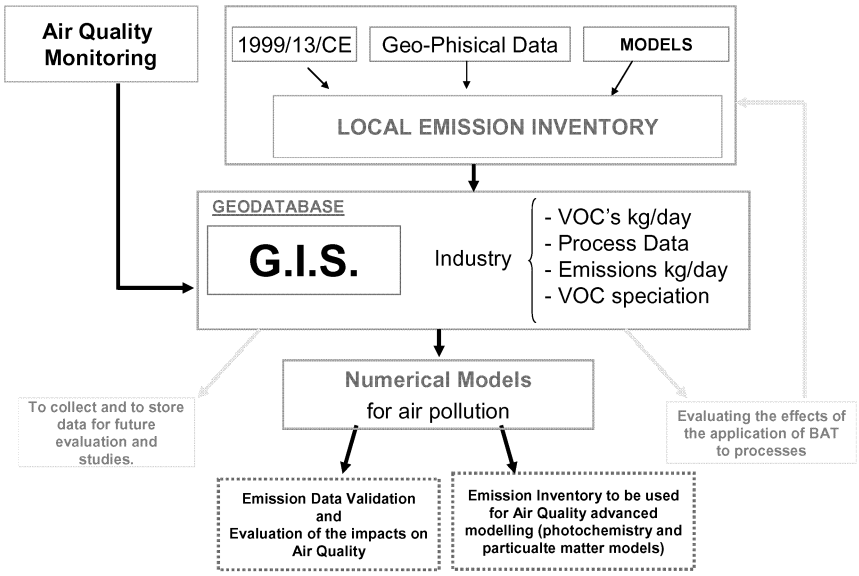

Figure 2 Scheme of the methodological approach developed for the VOC's study in Santa Croce.

3. Analysis and Result

3.1 Emission Inventory

The composition of every product used by each tanner were analysed by the safety data sheet SDS and create the emission inventory database of the VOC's, SAROAD 97 classification.

The organic compound, after some approximation concerning the product used in very low quantity respect the total VOC, result to be 151, divided in 84 water soluble compound WSOC's and 67 insoluble WINSOC's.

It was possible to compute the VOC's emissions that represent about 23,4 tons/day divided in 15,8 ton/day of water soluble organic compound, calculated with a developed mass balance algorithm taking into account solubility properties of compounds, and 6,5 ton/day of insoluble compound which passed through the abatement equipment without to be absorb and leaked directly in air. Figure 3 shows how the quantity of Ethyl Alcohol, Propylene Glycol, Acetone and Isopropyl Alcohol represent more than 70% of soluble compound used in the Leather District. While about insoluble compound we can observe which 87% of total quantity is composed by n–Butyl acetate and Toluene.

The local emission inventory contain for each tanner the single process description and the product used; in this way is possible to monitor the emissions and change quickly the information included when an improvement occurred. An important results is the possibility to compare the calculated data of the local inventory with ones estimated by I.R.S.E (2000) , the Regional Inventory of the Sources of Emissions in atmosphere,

with the aim to describes in detail the industrial sources of VOC. As results of this comparison it was possible to identify that IRSE under-estimate the VOC emissions by 31 %wt. In addition, the maximum spatial resolution of the IRSE database is 1km x 1km while in this study we perform single point chimney emissions data reconstruction, an example is shown in figure 4 where emission sources georeferenced allowed to create a chromatic map where it's possible to localize immediately the higher emissions flux of VOC's in the Leather District.

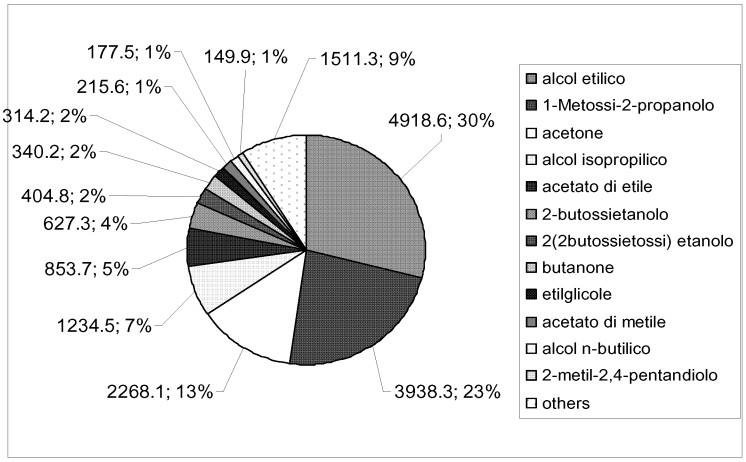

Figura 3a Water Solubile Organic Compound in each plot the quantities are expressed in [kg/day] ; [wt%].

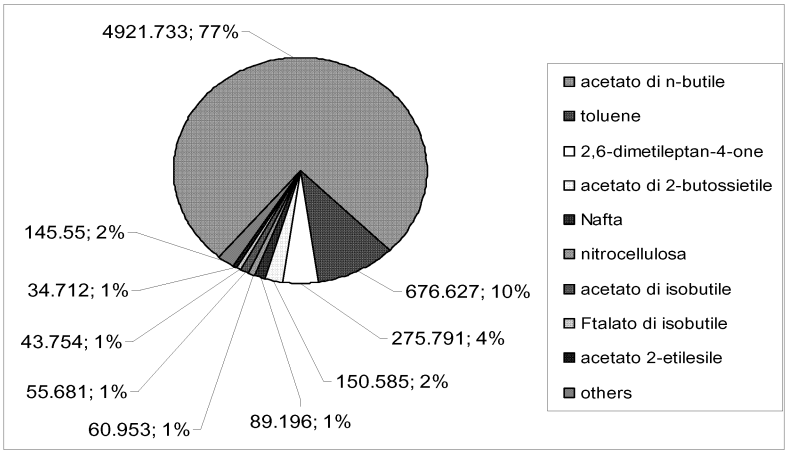

Figura 3b Water Insoluble Organic Compound in each plot the quantities are expressed in [kg/day] ; [wt%].

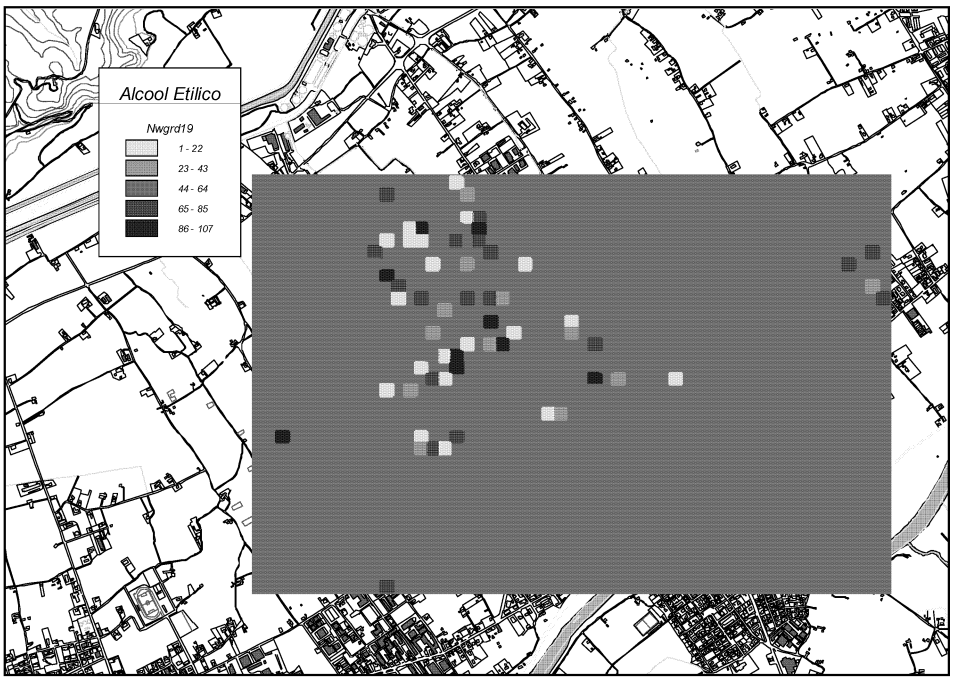

Figure 4 Chromatic map of Ethyl Alcohol emissions [kg/day] in Santa Croce sull'Arno

Another results of the proposed approach is the possibility to estract the VOC's data from the geodatabase to be employed to calculate the VOC contribution to the Secondary Organic Aerosol Formation or Ozone concentration by the application of advanced numerical modelling systems. For this reason we utilized the CBIV Chemical Lumped Mechanism to speciate the VOC emission and to build an emission inventory which can be implemented to chemical transport model as CAMx. The output of the CBIV was a speciated VOC Inventory where for each industrial sources is described the emissions. In the table below are described the total amount of every CBIV group expressed in Kmoli/day for the Santa Croce district.

Table 1 Amount of VOC emissions in CBIV groups for the Santa Croce district [Kmole per day].

	OLE	PAR	TOL	XYL	FORM	ALD2	OPEN	MEOH	ETOH	NTR
Santa Croce	0.03	583.67	7.28	0.37	58.62	48.07	0.02	4.34	141.65	0.05

3.2 Data Validation

Calpuff Model System , Scire (2000) is the numerical model utilized in this study to simulate the emission dispersion in air and their contribution to air quality on May-June 2006. For the numerical simulations we identified toluene as tracer of the tanners emissions in San Romano for this study used to compare the predicted concentration obtained by the VOC estimated data emissions with a data set of measures collected during an air quality monitoring campaign focused on tanners emissions in Santa Croce during 2006.

The meteorological data are acquired by the meteorological stations located in the District. Calpuff model System is suitable for simulations in areas characterized by complex orography, as in the Leather District, where the choice of using it is a good compromise between simulation detail, computational cost and complexity for both the orography and the meteorological condition.

The monitoring campaign for the identification of Toluene concentration was effectuated by positioning the instrumentation, BTX meter VOC 71M, in four points in the territory, chosen considering the meteorology site supplemented by the frequency of local people complaints about odorous emission of the tanneries. In fact, considering that in summer, during the daily band of greater radiation, the winds typical come from the south west in Santa Croce, and then tack back toward the northeast at the end of the day, it was chosen to place the instrument, firstly where the winds from the south east exert greater influence, and secondly where the weather situation is the opposite. In both cases the positions are outside the tanneries zone, so it is possible take the overall effect of emissions in the area and to consider if the estimated quantities of toluene obtained from the model was a good approximation.

The concentration estimated, using the Calpuff model system applied to the stack emissions of the tanners, are in good agreement to the value sampled by the instruments. Even if the results should be considered only as a first step to validate the VOC Inventory concerning the Toluene and then to be extrapolated to the total VOC's emitted.

The following figure 5 has been selected as example of the obtained results and it shows that the concentration profiles of the calculate data (gray lines) with Calpuff is in good agreement to measured data (blue lines).

From the picture of figure 5 it was also possible to verify how the predicted data underestimate the toluene concentration referring to the measured concentration, in the first and in the final part of the day, this could be caused by the contribution of traffic emission sources, in fact in the numerical simulation we considered only industrial source. Otherwise the picture shows that the model individuate the maximum value of concentration registered. A large part of the simulations effectuated demonstrate that the resolution and the approximation applied to compile the VOC Inventory individuate a good data collection quality and it was been possible to validate it.

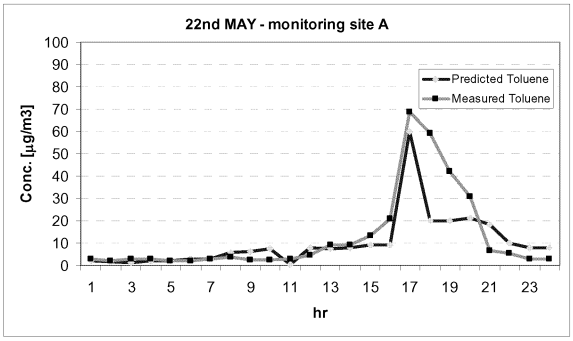

Figure 5 Comparison by predicted concentration and measured of toluene.

4. Conclusions

Through this study it was possible to develop a Local Emissions Inventory of VOC's which allowed to define in details the Leather District VOC's emission scenario. The results of this work define the first important step for the following consideration on how to operate for the reduction of the VOC emissions: knowing the emissions composition is more probably better to operate to improve the industrial plant design, for the abatement system or to research a mixture of organic compound utilized concerning to improve the air quality.

In conclusion the criterions to develop the Local Inventory and the data processing, utilized for Leather District, could be adopt to integrate the regional situation and to propose successively consideration using chemical transport model to value the contribution of VOC's for photochemical pollutants formation.

5. References

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